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• **Plessis, Caroline**  
**8051 Zürich (CH)**  
• **Derrer, Samuel**  
**8117 Fällanden (CH)**

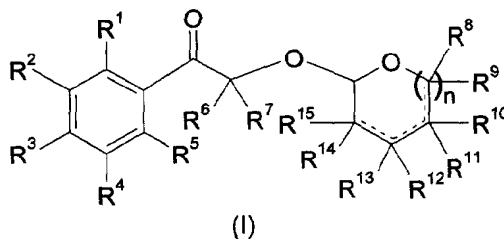
(71) Applicant: **Givaudan SA**  
**1214 Vernier-Genève (CH)**

(74) Representative:  
**Patentanwälte Schaad, Balass, Menzl & Partner**  
**AG**  
**Dufourstrasse 101 Postfach**  
**8034 Zürich (CH)**

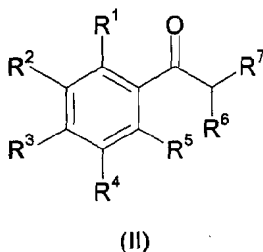
(72) Inventors:  
• **Gautschi, Markus**  
**4314 Zeiningen (CH)**

(54) **Fragrance precursors**

(57) The present invention refers to fragrance precursors of formula I

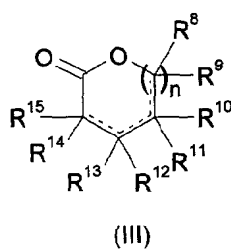


for a fragrant ketone of formula II



and a fragrant lactone of formula III.

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The substituents in this formula are defined in claim 1. These fragrance precursors are useful in perfumery, especially in the fine and functional perfumery.

## Description

[0001] The present invention relates to fragrance precursors for a fragrant ketone and a fragrant lactone.

[0002] A principal strategy currently employed in imparting odors to consumer products is the admixing of the fragrance directly into the product. There are, however, several drawbacks to this strategy. The fragrance material can be too volatile and/or too soluble, resulting in fragrance loss during manufacturing, storage, and use. Many fragrance materials are also unstable over time. This again results in loss during storage.

[0003] In many consumer products it is desirable for the fragrance to be released slowly over time. Micro-encapsulation and inclusion complexes with cyclodextrins have been used to help decrease volatility, improve stability and provide slow-release properties. However, these methods are for a number of reasons often not successful. In addition, cyclodextrins can be too expensive.

[0004] It is therefore desirable to have a fragrance delivery system which is capable of releasing the fragrant compound or compounds in a controlled manner, maintaining a desired smell over a prolonged period of time.

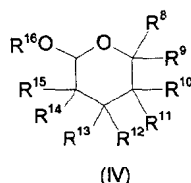
[0005] Precursors for the delivery of organoleptic compounds, especially for flavours, fragrances and masking agents, are described in EP-A 0 936 211. This delivery system releases one or more odoriferous compounds upon exposure to light and/or UV irradiation. Using this system in various consumer products leads to a prolonged perception of the fragrant compound(s) to be released.

[0006] WO 99/60990 describes fragrance precursors which release fragrant alcohols, aldehydes or ketones upon exposure to light. Perfuming compositions comprising these fragrance precursors can be used in various consumer products such as detergents, fabric softeners, household products, hair-care products etc..

[0007] Many fragrant compounds with odors accepted by the public are lactones. In fragrance compositions these lactones play an important role in imparting the fruity aspects of the perfume. Such lactones are fast hydrolysed in alkaline environment, thereby losing the fragrant characteristic and, consequently, the fruity aspect of the perfume. Therefore, they are of limited use for laundry products, especially detergents.

[0008] Certain compounds of formula I are known.

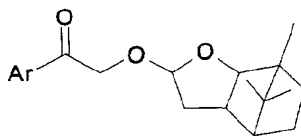
[0009] Cyclic acetals of the formula IV



with all of  $R^8$  to  $R^{15}$  being H, and  $R^{16}$  being the residue of an organic alcohol and serve as a protective group for alcohols (Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, 2<sup>nd</sup> ed.; John Wiley and Sons: New York, 1991, p31).

[0010] A compound of formula I with  $n = 1$ ,  $R^8 = C_6$ , and  $R^1$  to  $R^7$  as well as  $R^9$  to  $R^{15} = H$  has been used as an intermediate in a natural product synthesis (Dixon et al., *Synlett*, 1998, 1093-1095).

[0011] A further compound



is used as substrates in a diastereoselective reduction, wherein the cyclic acetal is used as chiral auxiliaries (e.g. Noe et al., *Angew. Chem.* 1988, 100, 1431-1433).

[0012] However, none of the above references discloses or suggests that the above mentioned compounds have the characteristics of fragrance precursor.

[0013] Object of the present invention is to provide fragrance precursors which are stable in alkaline environment, especially in laundry products.

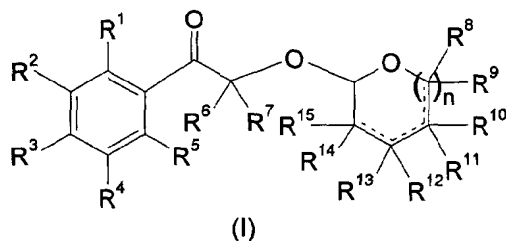
[0014] A further object of the present invention is to provide non-volatile precursors for volatile fragrant lactones.

[0015] Also an object of the present invention is to provide fragrance precursors with high substantivity.

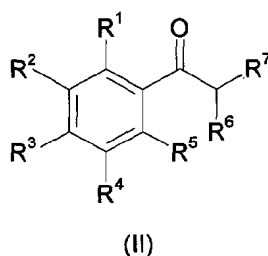
[0016] A further object of the present invention is to provide fragrance precursors which are activated and cleaved by light.

[0017] Also an object of the present invention is to provide fragrance precursors with slow release properties.

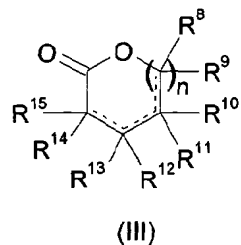
[0018] The present invention relates to fragrance precursors of formula I



the dotted lines indicating one or two optional double bonds in the cyclic acetal, which upon exposure to light, and in particular daylight, release a fragrant ketone of formula II



and a fragrant lactone of formula III



containing not more than 20 carbon atoms, wherein

R<sup>1</sup> to R<sup>5</sup> represent independently H, -NO<sub>2</sub>, branched or linear C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl or C<sub>1</sub>-C<sub>4</sub>-alkoxy,

R<sup>1</sup> and R<sup>2</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>3</sup> and R<sup>4</sup> and R<sup>4</sup> and R<sup>5</sup> may form together one or two aliphatic or aromatic rings, these rings may optionally contain branched or linear C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkenyl or C<sub>1</sub>-C<sub>4</sub>-alkynyl residues, and the above rings and residues may comprise one or more oxygen atoms,

R<sup>6</sup> and R<sup>7</sup> are independently H, branched or linear C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, and R<sup>6</sup> or R<sup>7</sup> may form with either R<sup>1</sup> or R<sup>5</sup> a carbocyclic ring optionally substituted by an aliphatic residue,

n is either 0 or 1,

$R^8$  to  $R^{15}$  are independently H, branched or linear  $C_1$ - $C_{15}$ -alkyl,  $C_1$ - $C_{15}$ -alkenyl,  $C_1$ - $C_{15}$ -alkynyl or  $C_1$ - $C_4$ -alkoxy,

they may form together one or more aliphatic or aromatic rings, these rings may optionally contain branched or linear  $C_1$ - $C_{10}$ -alkyl,  $C_1$ - $C_{10}$ -alkenyl or  $C_1$ - $C_{10}$ -alkynyl residues, and the above rings and residues may comprise one or more oxygen atoms,

and  
branched carbon chains also comprise multiple branched chains.

[0019] The present invention also relates to the compounds of formula I.

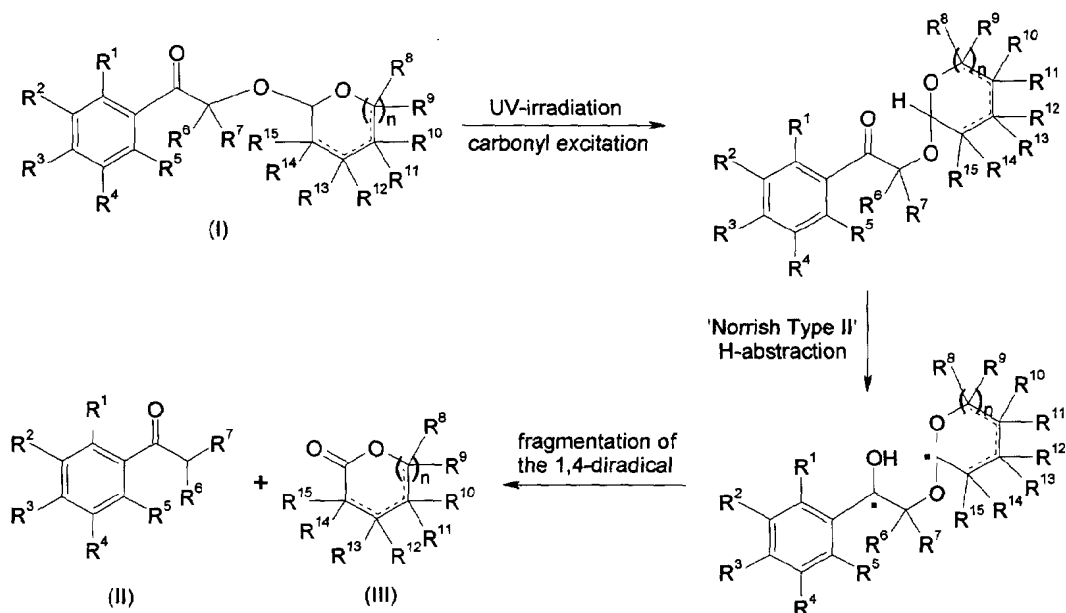
[0020] The fragrance precursors of formula I release upon exposure to light volatile fragrant lactones of formula III and fragrant ketones of formula II. Since the precursors of the invention are stable in alkaline environment and show high substantivity, they are excellently adapted for detergent and laundry use.

[0021] The fragrance precursors of the present invention are slowly cleaved when exposed to light, in particular daylight. Upon absorption of energy from said light, the phenacyl acetals undergo a Norrish Type II photoreaction which leads to the release of a fragrant ketone of formula II and a fragrant lactone of formula III.

[0022] The release of the above mentioned fragrant compounds occurs for example upon exposure to sunlight penetrating through ordinary windows and being not particularly rich in UV irradiation. It is needless to say that upon exposure to bright sunlight, in particular outdoors, the release of the fragrant compounds of formula II and III will occur faster and to a greater extent than upon exposure to room light inside a building. The cleavage of the precursors of the present invention can also be initiated by an appropriate lamp, for example a sun tanning lamp.

[0023] It is known that phenacyl glycosides undergo a Norrish Type II photoreaction leading to gluconolactones and the corresponding aryl ketone (Brunckova and Crich, *Tetrahedron*, 1995, 51, 11945-11952). However, it has not been described or suggested to use such phenacyl acetals as fragrance precursors, which are capable of releasing a fragrant ketone and a fragrant lactone over a prolonged period.

[0024] The photoreaction of the fragrance precursors of formula I involves in a first step the absorption of light by the keto-group followed by abstraction of the acetal-H atom and subsequent cleavage of the resulting 1,4-diradical (Scheme A). It has been found that the aromatic residue of the fragrance precursors plays an important role in this photoreaction as it influences the absorption maximum  $\lambda_{max}$  of the keto-group. Therefore, the cleavage properties of the fragrance precursors can be modified by variation of the substituents  $R^1$  to  $R^5$ .



Scheme A

Fragrant aryl alkyl ketones of formula II are well known to those skilled in the art. A fragrant ketone of formula II is a compound known to a person skilled in the art as being a useful ingredient for the formulation of perfumes or perfumed articles. Non-limiting examples of said aryl alkyl ketones are acetanisole (1-(4-methoxyphenyl)-ethanone) [Givaudan Roure (International) SA, Vernier, Switzerland], acetophenone (1-phenyl-ethanone) [Haarmann & Reimer GmbH, Germany], Crisolide® (4-acetyl-6-tert-butyl-1,1-dimethyl-indan) [Givaudan Roure (International) SA, Vernier, Switzerland], Dimethyl acetophenone (1-(2,4-dimethylphenyl)-ethanone) [Fluka AG, Buchs, Switzerland], Fixolide® (1-(5,6,7,8-tetrahydro-3',5',5',6',8',8'-hexamethyl-2-naphthalenyl)-ethanone) [Givaudan Roure (International) SA, Vernier, Switzerland], Florantone T® (1-(5,6,7,8-tetrahydro-2-naphthalenyl)-ethanone) [Takasago Perfumery Co., Japan], Grassenone 34® (3-methyl-1-(4-methylphenyl)-4-hexen-1-one) [Keemia Institute, Tallin USSR], isopropylindanone (2-(1-methylethyl)-indanone) [Givaudan Roure (International) SA, Vernier, Switzerland], Lavonax® (1-phenyl-4-penten-1-one) [International Flavors & Fragrances, USA], Musk F (5-acetyl-1,1,2,3,3-pentamethyl-indane) [CNNP], Musk ketone® (4-tert-butyl-3,5-dinitro-2,6-dimethyl-acetophenone) [Givaudan Roure (International) SA, Vernier, Switzerland], Novalide® (1,6,7,8-tetrahydro-1',4',6',6',8',8'-hexamethyl-indacen-3(2H)-one) [Givaudan Roure (International) SA, Vernier, Switzerland], Oranger Crystals® (1-(2-naphthalenyl)-ethanone) [Givaudan Roure (International) SA, Vernier, Switzerland], Orinox® (1-[4-(1,1-dimethylethyl)-2,6-dimethylphenyl]-ethanone) [Polak's Frutal Works BV, Netherlands], Phantolide® (1-(2,3-dihydro-1',1',2',3',3',6'-hexamethyl-1H-inden-5-yl)-ethanone) [Polak's Frutal Works BV, Netherlands], propiophenone (1-phenyl-propanone) [Haarmann & Reimer GmbH, Germany], Traseolide 100® (1-[2,3-dihydro-1',1',2',6'-tetramethyl-3-(1-methylethyl-1H-inden-5-yl)-ethanone) [Quest International, Netherlands], Vernolide® (1-(5,6,7,8-tetrahydro-3',5',5',8',8'-pentamethyl-2-naphthalenyl)-ethanone) [Givaudan Roure (International) SA, Vernier, Switzerland], Versalide® (1-(5,6,7,8-tetrahydro-3'-ethyl-5',5',8',8'-tetramethyl-2-naphthalenyl)-ethanone) [Givaudan Roure (International) SA, Vernier, Switzerland], Vitalide® (1-(hexahydrodimethyl-1H-benzindenyl)-ethanone) [Takasago Perfumery, Japan].

**[0025]** It is obvious to the person skilled in the art that the above list is illustrative and that the present invention relates to many other fragrant ketones of formula II.

**[0026]** Additional fragrant ketones of formula II are e.g. described in "Perfume and Flavor Chemicals", S. Arctander Ed., Vol. I & II, Allured Publishing Corporation, Carol Stream, USA, 1994 and in "Common Fragrance and Flavor Materials", K. Bauer, D. Garbe and H. Surburg, Eds., Wiley-VCH, 3<sup>rd</sup> Edition, Weinheim, 1997.

**[0027]** Fragrant lactones of formula III, represent an important class of perfumery raw materials and comprise compounds of a vast structural variety. Fragrant lactones of formula III contribute to the odor and aroma of various fruits and are known to be useful ingredients for the formulation of perfumes or perfumed articles. In the following list such lactones are given as examples.

**[0028]** Most of the lactones of formula III are gamma-lactones with  $n = 0$ . They are derived from gamma-hydroxy-carboxylic acids and examples for such lactones of formula III include gamma-valerolactone, gamma-octalactone, Prunolide® (gamma nonalactone) [Givaudan Roure (International) SA, Vernier, Switzerland], gamma-decalactone, Peach Pure® (gamma-undecalactone) [Givaudan Roure (International) SA, Vernier, Switzerland], gamma-dodecalactone, 5-(3Z-hexenyl)-dihydro-2(3H)-furanone and 5-(1,5-dimethyl-4-hexenyl)-dihydro-2(3H)-furanone.

**[0029]** Alpha-monosubstituted gamma-lactones of formula III with  $n = 0$  are for example 2-heptylbutyrolactone and 2-hexylbutyrolactone.

**[0030]** Bisubstituted gamma-lactones of formula III with  $n = 0$  are for example Lactone of cis-Jasmone® [5-(3Z-hexenyl)-dihydro-5-methyl-2(3H)-furanone] [Bedoukian Inc., USA], Lactojasmone® (5-hexyl-dihydro-5-methyl-2(3H)-furanone) [Haarmann & Reimer GmbH, Germany], Whiskey Lactone [Fontarome Chemical Inc., USA], 4-methyl-5-pentyl-dihydro-2(3H)-furanone, and 3-acetyl-5-butyl-dihydro-2(3H)-furanone.

**[0031]** Bisubstituted spiro-bicyclic gamma-lactones of formula III with  $n = 0$ , are for example Laitone® {8-(1-methylethyl)-1-oxaspiro[4.5]-decan-2-one} [Givaudan Roure (International) SA, Vernier, Switzerland], Ethyl Laitone® {8-ethyl-1-oxaspiro[4.5]-decan-2-one} [Givaudan Roure (International) SA, Vernier, Switzerland] and Methyl Laitone® {8-methyl-1-oxaspiro[4.5]-decan-2-one} [Givaudan Roure (International) SA, Vernier, Switzerland].

**[0032]** Another important class of the lactones of formula III are the delta-lactones with  $n = 1$ . They are derived from the delta-hydroxy-carboxylic acids and examples for such lactones of formula III include delta-hexalactone, delta-heptalactone, delta-octalactone, delta-nonolactone, delta-decalactone, delta-undecalactone, delta-dodecalactone and delta-tetradecalactone. Further examples comprise Jasmolactone {6-(3E-pentenyl)-tetrahydro[2H]pyran-2-one} [Firmenich S.A., Switzerland], Jasmolactone Extra C {6-(3Z-hexenyl)-tetrahydro[2H]pyran-2-one} [Bedoukian Inc., USA] and 6-(2Z-pentenyl)-tetrahydro[2H]pyran-2-one.

**[0033]** Multiple-substituted monocyclic lactones of formula III are the delta-lactones with  $n = 1$ . Such lactones of formula III are for example 4,4,6-trimethyltetrahydropyran-2-one and 5-butyl-5-ethyltetrahydropyran-2-one.

**[0034]** Multiple-substituted polycyclic lactones of formula III are the delta-lactones with  $n = 1$ . Such lactones of formula III are for example Florex® (6- or 7-ethylideneoctahydro-5,8-methano[2H]-1-benzopyran-2-one) [Firmenich S.A., Switzerland], Lactoscatone® (hexahydro-3,5,5-trimethyl-3,8a-ethano[8aH]-1-benzopyran-2(3H)one) [DRAGOCO Gerberding & Co. AG, Germany] (Dragoco), Coumarin, Dihydrocoumarin [Givaudan Roure (International) SA, Vernier, Switzerland].

zerland], and Octahydrocoumarin.

**[0035]** Some of the lactones of formula III described above, which are of pleasant odor, are rather volatile. This is especially true for low molecular weight lactones being substituted by aliphatic chains exhibiting typical fruity odors.

**[0036]** The fragrance precursors of the present invention are not, or only slightly, volatile. The fragrant ketone of formula II and the fragrant lactone of formula III are released only upon exposure to light, and especially daylight. The photochemical cleavage provides over days and weeks perceptible amounts of the fragrant compounds. The period depends inter alia on the amount or concentration of the precursor applied, the duration of exposure to light, its intensity and its wavelength.

**[0037]** Fragrant lactones of formula III are prone to undergo hydrolysis, especially in alkaline products such as detergents, into the hydroxy fatty acids salts, which exhibit enhanced water solubility and to a great extent are washed away in the washing/cleaning process. This results in considerable loss of perfume and in particular the fruity notes.

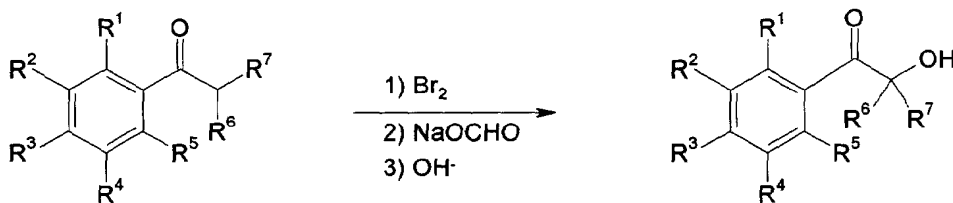
**[0038]** Today's consumers select a certain product not only based on performance but also based on the odor. From the foregoing it is evident that systems for introducing a variety of fragrance accords to products having alkaline pH are desirable. The fragrance precursors of the present invention have the advantage that they are not or only slightly volatile and chemically stable in consumer products having alkaline and neutral pH. A precursor of formula I added to a powder detergent, is stable in the detergent powder throughout storage. During the washing cycle (alkaline pH) and the rinsing cycle (neutral pH) the precursor is deposited on the fabric surface. It is only upon exposure of the fabric to light, for example during line drying in the sun, that the release of the fragrant ketone of formula II and the fragrant lactone of formula III is started.

**[0039]** It has been mentioned above that lactones of formula III, and especially the aliphatic low molecular weight ones, are rather volatile compounds. Furthermore, they are water soluble and are, therefore, lost to some extent during the washing/rinsing cycle if introduced directly into detergents.

**[0040]** The fragrance precursors of formula I have the advantage that they have good substantivity on different substrates, especially on fabrics. Furthermore, the precursors are not or only slightly volatile, thus no loss occurs during storage. With the precursors of the present invention highly volatile lactones of formula III with low substantivity are successfully applied to achieve a long lasting pleasant odor. The volatile lactones are produced in situ after application of the precursors of formula I onto a fabric during the washing cycle.

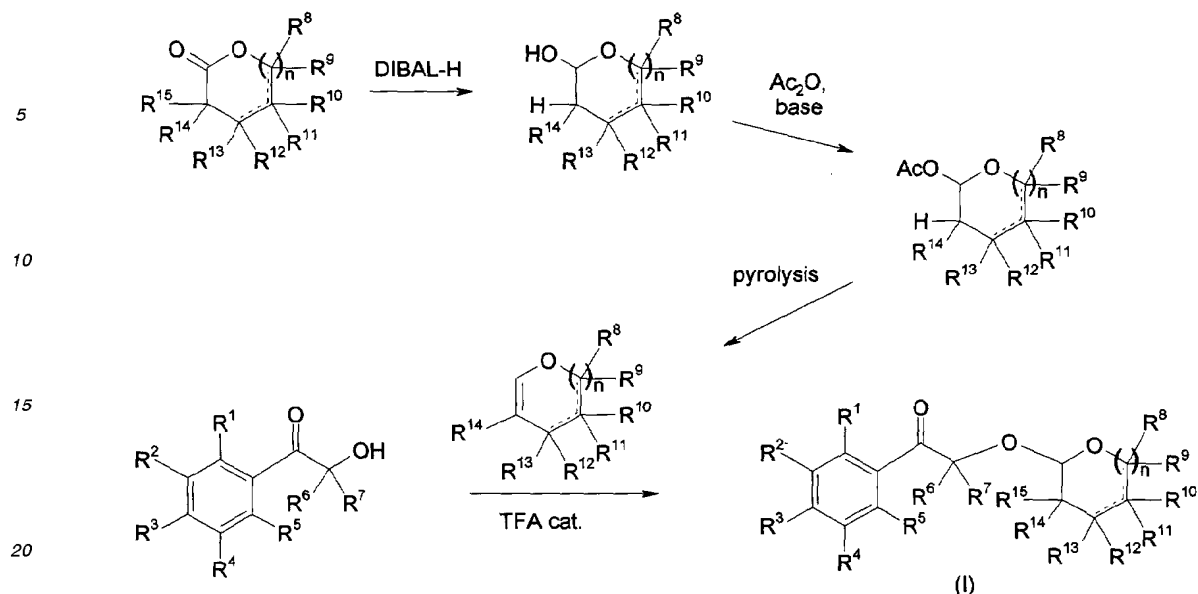
**[0041]** In the precursors of the invention the moiety derived from a fragrant ketone of formula II brings three advantages: it introduces stability as well as substantivity to the precursors of formula I and upon activation by light exhibits fragrant properties.

**[0042]** The fragrance precursors of the present invention are advantageously prepared via two methods. Both methods use an  $\alpha$ -hydroxy-ketone as starting material. The latter is prepared by bromination of the corresponding fragrant ketone followed by sodium formate treatment and subsequent hydrolysis as shown in scheme I:



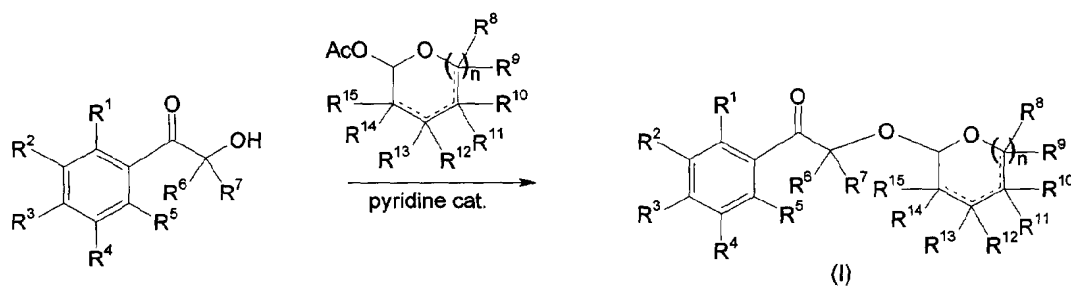
Scheme I

Then according to the first method the  $\alpha$ -hydroxy-ketone intermediate is reacted under acid conditions with a cyclic vinyl ether to the desired precursor of formula I. The cyclic vinyl ether is obtained from the corresponding lactone after reduction to the lactol, followed by acetylation and thermal elimination of acetic acid. For this method, either  $R^{14}$  or  $R^{15}$  need to be H. The synthesis is illustrated in scheme II:



Scheme II

30 **[0043]** According to the second method the  $\alpha$ -hydroxy-ketone is reacted under slightly basic conditions with the afore mentioned lactol acetate. This method is particularly suitable for lactones with both,  $R^{14}$  and  $R^{15}$ , not being H. The synthesis via this route is illustrated in scheme III:



Scheme III

50 **[0044]** Preferred precursors of the present invention are compounds releasing a lactone of formula III wherein  $n = 0$ ,  $R^{10}$  is an aliphatic residue having 1 to 15 carbon atoms and  $R^{11}$  to  $R^{15}$  are H. Most preferred precursors are those releasing a lactone derived from gamma-hydroxy fatty acids having 4 to 14 carbon atoms.

**[0045]** Other preferred precursors include compounds wherein  $n = 0$ , one substituent of  $R^{11}$  to  $R^{15}$  is an aliphatic residue having 1 to 15 carbon atoms and the others being H. Most preferred compounds are those releasing a lactone wherein the said residue is  $R^{15}$  having 1 to 10 carbon atoms.

**[0046]** Other preferred precursors include compounds wherein  $n = 0$ , two or more substituents of  $R^{10}$  to  $R^{15}$  are aliphatic residues having 1 to 15 carbon atoms and the others being H. Most preferred compounds are those wherein  $R^{10}$  to  $R^{11}$  are aliphatic residues having 1 to 10 carbon atoms.



**[0047]** Other preferred precursors include compounds wherein  $n = 0$  and two or more substituents of  $R^{10}$  to  $R^{15}$  are residues having 1 to 15 carbon atoms and form together one or more carbocyclic ring(s), which may optionally be substituted with one or more aliphatic residue(s) having 1 to 10 carbon atoms. Most preferred compounds are spirocyclic structures wherein  $R^{10}$  to  $R^{11}$  form together a carbocyclic ring which is further substituted with one or more aliphatic residues having 1 to 10 carbon atoms.

**[0048]** Other preferred precursors of the present invention are compounds releasing a lactone of formula III wherein  $n = 1$ ,  $R^8$  is an aliphatic residue having 1 to 15 carbon atoms and  $R^9$  to  $R^{15}$  are H. Most preferred precursors are those releasing a lactone derived from delta-hydroxy fatty acids having 5 to 14 carbon atoms.

**[0049]** Other preferred precursors include compounds wherein  $n = 1$ , two or more substituents of  $R^8$  to  $R^{15}$  are aliphatic residues having 1 to 15 carbon atoms and the others being H. Most preferred compounds are 4,4,6-trimethyltetrahydropyran-2-one and 5-butyl-5-ethyltetrahydropyran-2-one.

**[0050]** Other preferred precursors include compounds wherein  $n = 1$  and at least two substituents of  $R^8$  to  $R^{15}$  are residues having 1 to 15 carbon atoms and form together one or more carbocyclic ring(s), which may optionally be substituted with one or more aliphatic residues having 1 to 10 carbon atoms. Most preferred compounds are Florex® (6- or 7-ethylideneoctahydro-5,8-methano[2H]-1-benzopyran-2-one) [Firmenich S.A., Switzerland], Lactoscatone® (hexahydro-3,5,5-trimethyl-3,8a-ethano[8aH]-1-benzopyran-2[3H]one) [DRAGOCO Gerberding & Co. AG, Germany] (Dragoco), Coumarin, Dihydrocoumarin [Givaudan Roure (International) SA, Vernier, Switzerland], and Octahydrocoumarin.

**[0051]** Other preferred precursors include compounds wherein at least one of the residues  $R^6$  or  $R^7 = H$ . Most preferred are compounds wherein  $R^6$  and  $R^7 = H$ . Upon cleavage of these precursors a fragrant ketone of formula II is released wherein said ketone is an aryl methyl ketone.

**[0052]** Other preferred precursors include compounds wherein  $R^6$  and  $R^7 = H$  and  $R^1$  to  $R^5$  represent independently hydrogen,  $-NO_2$ , linear or branched  $C_1$ - $C_6$  alkyl, alkenyl, alkynyl, and  $C_1$ - $C_4$  alkoxy. Most preferred compounds are those releasing a fragrant ketone of formula II wherein the fragrant ketone is selected from 1-phenyl-ethanone, 2,4-dimethylphenylethanone, 1-[4-(1,1-dimethylethyl)-2,6-dimethylphenyl]-ethanone, 1-(4-tert-butyl-3,5-dinitro-2,6-dimethyl)-ethanone and 1-(4-methoxyphenyl)-ethanone.

**[0053]** Other preferred precursor include compounds wherein  $R^1$  and  $R^2$ ,  $R^2$  and  $R^3$ ,  $R^3$  and  $R^4$ , and  $R^4$  and  $R^5$  form together one or two ring(s), which is (are) aliphatic and/or aromatic. The ring respectively these rings may optionally contain substituted or unsubstituted  $C_1$ - $C_4$  alkyl, alkenyl, alkynyl residues and may comprise one or more oxygen atoms. Most preferred compounds are those releasing a fragrant ketone of formula II wherein the fragrant ketone is selected from 1-(2-naphthalenyl)-ethanone, 4-acetyl-6-tert-butyl-1,1-dimethyl-indan, 1-(5,6,7,8-tetrahydro-3',5',6',8'-hexamethyl-2-naphthalenyl)-ethanone, 1-(5,6,7,8-tetrahydro-3',5',5',8',8'-pentamethyl-2-naphthalenyl)-ethanone, 1-(5,6,7,8-tetrahydro-3'-ethyl-5',5',8',8'-tetramethyl-2-naphthalenyl)-ethanone, 1-(2,3-dihydro-1',1',2',3',3',6'-hexamethyl-1H-inden-5-yl)-ethanone, 1-[2,3-dihydro-1',1',2',6'-tetramethyl-3-(1-methylethyl)-1H-inden-5-yl]-ethanone], 5-acetyl-1,1,2,3,3-pentamethylindane, 1-(5,6,7,8-tetrahydro-2-naphthalenyl)-ethanone.

**[0054]** Since the compounds of formula I, upon exposure to light are cleaved and provide a fragrant ketone of formula II and a fragrant lactone of formula III, they permit the development of useful consumer products with enhanced fragrant properties, especially having long lasting pleasant odor. Therefore, the present invention also relates to the use of all compounds of formula I as precursors for fragrant compounds.

**[0055]** The fragrance precursors of the present invention can be used in any product in which a prolonged and defined release of the above mentioned fragrant compounds is desired. Therefore, these precursors are especially useful in functional perfumery, in products which are exposed to sunlight, during or after application.

**[0056]** The compounds of the present invention can act as fragrance precursors in functional and fine perfumery i. e. in fine fragrances, industrial, institutional, home and personal care products. Industrial, institutional and home cleaning products to which the fragrance precursors can be added are all kinds of detergents, window cleaners, hard surface cleaners, all purpose cleaners and furniture polishes. The products can be liquids or solids, such as powders or tablets. Fabrics and surfaces treated with a product comprising a fragrance precursor of the present invention will diffuse a fresh and clean odor upon exposure to light much longer than when cleaned with a conventional cleaner. Fabrics or cloths washed with such detergents will release the fragrant compounds even after having been stored for weeks in a dark place, e.g. a wardrobe.

**[0057]** The precursors of the present invention are also useful for application in all kinds of body care products. Especially interesting products are hair care products, for example shampoos, conditioners and hairsprays and skin care products such as cosmetic products and especially sun protection products.

**[0058]** The above mentioned examples are of course only illustrative and non-limiting. Many other products to which the precursors of the present invention may be added include soaps, bath and shower gels, deodorants and even perfumes and colognes.

**[0059]** The fragrance precursors of the present invention can be used alone or in combination with other fragrance ingredients, solvents or adjuvants known to those skilled in the art. Such ingredients are described, for example, in

"Perfume and Flavor Chemicals", S. Arctander, Ed., Vol. I & II, Allured Publishing Corporation, Carol Stream, USA, 1994 and include fragrance compounds of natural or synthetic origin and essential oils of natural products.

[0060] The amounts in which the precursors of formula I are incorporated in the various above-mentioned products vary within a wide range. The amounts depend on the nature of the fragrant compounds to be released, the nature of the product to which the precursors are added and the desired olfactory effect. The amounts used also depend on the co-ingredients in a given composition when the precursors of the present invention are used in admixture with perfuming co-ingredients, solvents or adjuvants. Typical concentrations are in the order of 0.01% to 5% by weight of the products.

[0061] The following non-limiting examples further illustrate the embodiments of the invention.

[0062] The following chemicals were obtained from commercial sources: bromo-acetonaphtone, bromo-acetanisole, sodium formate, diisobutyl-aluminum hydride (solution in hexanes), Jasmolactone®, Peach Pure®, Methyl Laitone®, acetic anhydride, triethylamine, pyridine, trifluoroacetic acid.  $\alpha$ -Bromo-Fixolide was prepared from Fixolide® according to R.M. Cowper, L.H. Davidson, *Org. Synth. Coll. Vol. II*, 1943, 480-481.

[0063] NMR: values of coupling constants  $J$  are given in Hertz (Hz).

## Example 1

### Preparation of Cyclic Phenacyl Acetals

#### 1. General procedure for the preparation of hydroxyacetophenones

[0064] A suspension of the corresponding bromo-acetophenone (0.05 mmol) and sodium formate (17 g, 0.25 mol, 5 eq.) in aqueous ethanol (85%, 150 ml) was heated at reflux until completion of the reaction (TLC). Most of the ethanol was evaporated and the mixture partitioned between MTBE (80 ml) and water (70 ml). The organic phase was separated and washed with aqueous  $\text{NaHCO}_3$  (sat.) and brine. Removal of the solvent in vacuo, after drying over  $\text{MgSO}_4$ , afforded a crude product as a solid which was recrystallised from ethanol.

#### 2-Hydroxy-1-(4-methoxy-phenyl)-ethanone

[0065] Obtained according to the general procedure.

mp 104-105 °C.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 3.48 (t, 1H,  $J$  4); 4.82 (d, 2H,  $J$  4); 6.95-7.0 (m, 2H); 7.85-7.95 (m, 2H).

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ , neat): 3415m, 2929w, 1672s, 1603s.

MS [ $m/z$  (EI)]: 166 ( $M^+$ , 4), 155 (100), 77 (28).

#### 1-(3,5,5,6,8,8-Hexamethyl-5',6',7',8'-tetrahydronaphthalen-2-yl)-2-hydroxy-ethanone

[0066] Obtained according to the general procedure.

mp 81-82 °C.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 1.0 (d, 3H,  $J$  6.8); 1.08 (s, 3H); 1.26 (s, 3H); 1.31 (s, 3H); 1.33 (s, 3H); 1.41 (dd, 1H,  $J$  13.2, 2.4); 1.63 (dd, 1H,  $J$  13.2, 13.2); 1.8-1.95 (m, 1H); 2.54 (s, 3H); 4.76 (s, 2H); 7.26 (s, 1H); 7.57 (s, 1H).

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ , neat): 3447w, 2963m, 2911m, 1675s, 1607w.

MS [ $m/z$  (EI)]: 274 ( $M^+$ , 3), 243 (100).

#### 2-Hydroxy-1-naphthalen-2-yl-ethanone

[0067] Obtained according to the general procedure.

mp 114-115 °C.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 3.59 (t, 1H,  $J$  4.4); 5.02 (d, 2H,  $J$  4.4); 7.55-7.7 (m, 2H); 7.85-8.0 (m, 4H); 8.43 (s, 1H).

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IR ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ , neat) : 3428m, 3391m, 3051w, 2931w, 1680s, 1627m.

MS [ $m/z$  (EI)] : 186 ( $M^+$ , 12), 155 (75), 127 (100), 40 (26), 28 (41).

### 2. General procedure for the preparation of lactols

[0068] The lactols were obtained by reduction of the corresponding lactone: a suspension of the lactone (0.1 mol) in toluene (150 ml) was cooled to  $-78\text{ }^{\circ}\text{C}$  ( $\text{CO}_2/\text{acetone}$ ) and treated with a solution of DIBAL-H ( $\sim 1\text{ M}$  in hexanes, 110 ml, 0.11 mol, 1.1 equivalents). After the reaction was finished, methanol (85 ml) was slowly added and the reaction mixture allowed to warm to room temperature. Then, a solution of potassium sodium tartrate (Rochelle's salt) (30% aq.) was added and the mixture stirred for 45 min, upon which the phases separated well. The aqueous phase was extracted with MTBE, and the combined organic layers were washed twice with potassium sodium tartrate (Rochelle's salt) (30% aq.) and dried over  $\text{MgSO}_4$ . The crude obtained after removal of the solvents was purified by distillation under reduced pressure to afford a colourless oil.

#### 8-Methyl-1-oxa-spiro[4.5]decan-2-ol

[0069] Obtained as a mixture of diastereomers (ratio 1:4) from Methyl Laitone® according to the general procedure.

bp<sub>0.06 Torr</sub>: 72-73  $^{\circ}\text{C}$ .

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 0.8-1.05 (m, 2H); 0.88 (d, 3H,  $J$  6.4); 1.2-1.55 (m, 4H); 1.6-1.75 (m, 2H); 1.8-2.1 (m, 5H); 3.67 (s, 0.2H); 3.83 (s, 0.8H); 5.50 (m, 1H).

IR ( $\nu_{\max}$ , neat,  $\text{cm}^{-1}$ ) : 3400mbr, 2925s, 2855m, 1774w.

MS [ $m/z$  (EI)]: 170 ( $M^+$ , 1), 152 (47), 113 (39), 108(28), 96 (25), 95 (100), 93 (31), 81 (70), 79 (29), 70 (22), 67 (46), 55 (46), 53 (20), 41 (37), 39 (27).

#### 5-Heptyl-tetrahydro-furan-2-ol

[0070] Obtained as a mixture of diastereomers (ratio 2:3) from Peach Pure® according to the general procedure.

bp<sub>0.07 Torr</sub>: 96-98  $^{\circ}\text{C}$ .

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 0.88 (t, 3H,  $J$  6.8); 1.2-1.5 (m, 11H); 1.5-1.65 (m, 1H); 1.65-1.8 (m, 1H); 1.8-1.9 (m, 1H); 1.9-2.0 (m, 1H); 2.0-2.17 (m, 1H); 2.98 (d, 0.4H,  $J$  2.4); 3.07 (d, 0.6H,  $J$  2.4); 3.95-4.02 (m, 0.4H); 4.15-4.25 (m, 0.6H); 5.45-5.5 (m, 0.4H); 5.52-5.6 (m, 0.6H).

IR ( $\nu_{\max}$ , neat,  $\text{cm}^{-1}$ ) : 3405mbr, 2926s, 2856m, 1780w.

MS [ $m/z$  (EI)]: 185 ( $M^+-\text{H}$ , 1), 87 (100), 69 (41), 55 (22), 43 (30), 41 (27).

#### 6-(Pent-3-enyl)-tetrahydro-pyran-2-ol

[0071] Obtained as a mixture of diastereomers (ratio 35:65) from Jasmolactone® according to the general procedure, without final distillation.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) : 1.1-1.25 (m, 0.35H); 1.25-1.4 (m, 0.65H); 1.4-1.75 (m, 7H); 1.75-1.9 (m, 2H); 2.0-2.2 (m, 2H); 2.3-2.37 (m, 0.65H); 2.42-2.5 (m, 0.35H); 2.9 (s, 0.35H); 3.37-3.45 (m, 0.65H); 3.52 (s, 0.65H); 3.9-4.0 (m, 0.35H); 4.69 (d, 0.65H,  $J$  9.2); 5.3 (s, 0.35H); 5.35-5.5 (m, 2H).

IR ( $\nu_{\max}$ , neat,  $\text{cm}^{-1}$ ) : 3394mbr, 2936m, 2857m, 1719m.

MS [ $m/z$  (EI)]: 170 ( $M^+$ , 1), 152 ( $M-\text{H}_2\text{O}$ , 23), 98 (36), 95 (21), 83 (22), 81 (48), 79 (25), 69 (23), 68 (26), 67 (40), 56 (24), 55 (100), 41 (41), 39 (26).

**3. General procedure for the preparation of the acetylated lactols.**

**[0072]** A cold (0°C) solution of the lactol (50 mmol) in dichloromethane (75 ml) was treated with acetic anhydride (9.5 ml, 100 mmol, 2 eq.) and triethylamine (13.9 ml, 100 mmol, 2 eq.). After stirring overnight at room temperature, the mixture was poured into cold water and the separated aqueous phase was extracted with MTBE. The combined organic layers were washed with water and brine, and dried over MgSO<sub>4</sub>. Removal of the solvents afforded a colourless oil which was used without further purification.

**Acetic acid 8-methyl-1-oxa-spiro[4.5]dec-2-yl ester**

**[0073]** Obtained according to the general procedure.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.9-1.05 (m, 2H); 0.89 (d, 3H, *J* 6.4); 1.3-1.45 (m, 2H); 1.45-1.6 (m, 2H); 1.7-1.95 (m, 5H); 2.0-2.2 (m, 2H); 2.02 (s, 3H); 6.24 (d, 1H, *J* 4.4).

**IR** (ν<sub>max</sub>, neat, cm<sup>-1</sup>): 2928m, 2857m, 1740s.

**MS** [m/z (EI)]: 212 (M<sup>+</sup>, 1), 152 (53), 108(28), 96 (24), 95 (100), 93 (31), 81 (70), 79 (28), 70 (22), 67 (41), 55 (34), 45 (23), 43 (36), 41 (31), 39 (24).

**Acetic acid 5-heptyl-tetrahydro-furan-2-yl ester**

**[0074]** Obtained as a mixture of diastereomers (ratio 45:55) according to the general procedure.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3H, *J* 6.6); 1.2-1.8 (m, 14H); 1.9-2.2 (m, 2H); 2.03 (s, 1.35H); 2.04 (s, 1.65H); 4.02-4.12 (m, 0.45H); 4.17-4.22 (m, 0.55H); 6.23 (m, 0.45H); 6.28 (m, 0.55H).

**IR** (ν<sub>max</sub>, neat, cm<sup>-1</sup>): 2927m, 2856m, 1780m, 1742s.

**MS** [m/z (EI)]: 228 (M<sup>+</sup>, 1), 168 (35), 84 (54), 83 (59), 82 (37), 81 (26), 71 (33), 70 (54), 69 (100), 68 (23), 67 (26), 57 (48), 56 (34), 55 (67), 43 (39), 41 (67), 39 (28), 29 (24).

**Acetic acid 6-pent-3-enyl-tetrahydro-pyran-2-yl ester**

**[0075]** Obtained as a mixture of diastereomers (ratio 1:1) according to the general procedure.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): 1.15-1.3 (m, 1H); 1.4-1.7 (m, 8H); 1.75-1.85 (m, 1H); 1.85-1.95 (m, 1H); 2.0-2.15 (m, 1H); 2.1 (s, 3H); 2.3-2.37 (m, 0.5H); 2.4-2.5 (m, 0.5H); 3.47-3.55 (m, 1H); 5.35-5.5 (m, 2H); 5.63 (m, 1H).

**IR** (ν<sub>max</sub>, neat, cm<sup>-1</sup>): 2940w, 1743m.

**MS** [m/z (EI)]: 212 (M<sup>+</sup>, 1), 95 (24), 81 (55), 79 (27), 68 (26), 67 (41), 57 (28), 55 (100), 53 (20), 45 (20), 43 (42), 41 (40), 39 (32), 29 (25).

**4. General procedure for the preparation of the cyclic vinyl ethers**

**[0076]** Cyclic vinyl ethers were obtained by pyrolysis: a solution of the acetyl derivative (50 mmol) in toluene (100 ml) was dropped through a hot (260 °C) vertical Pyrex® tube (32 cm in length, 2 cm in diameter) filled with Pyrex® Raschig rings (5 mm in height, 3 mm in diameter) under normal pressure. The reaction solution was collected in a cold flask (CO<sub>2</sub>/acetone) and washed with aq. NaHCO<sub>3</sub> (sat.) and brine. After drying over MgSO<sub>4</sub> and removal of the solvents, the crude was purified by distillation.

**8-Methyl-1-oxa-spiro[4.5]dec-2-ene**

**[0077]** Obtained according to the general procedure.

**bp**<sub>0.1 Torr</sub>: 50 °C (Kugelrohr).

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**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) : 0.90 (d, 3H, *J* 6.8); 0.95-1.1 (m, 2H); 1.25-1.65 (m, 5H); 1.65-1.85 (m, 4H); 4.75 (m, 1H); 6.25 (m, 1H).

**IR** ( $\nu_{\max}$ : neat, cm<sup>-1</sup>) : 2927s, 2855m, 1743m, 1621m.

**MS** [*m/z* (EI)]: 152 (M<sup>+</sup>, 54), 108 (30), 96 (26), 95 (100), 93 (33), 81 (76), 79 (30), 70 (23), 67 (44), 55 (35), 53 (20), 41 (31), 39 (26).

### 2-Heptyl-2,3-dihydro-furan

[0078]

**bp**<sub>12 mbar</sub>: 90-91 °C.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) : 0.88 (t, 3H, *J* 8); 1.2-1.45 (m, 10H); 1.5-1.6 (m, 1H); 1.65-1.75 (m, 1H); 2.2-2.3 (m, 1H); 2.65-2.72 (m, 1H); 4.47-4.55 (m, 1H); 4.84 (m, 1H); 6.26 (m, 1H).

**IR** ( $\nu_{\max}$ : neat, cm<sup>-1</sup>) : 2926s, 2856m, 1731w, 1619m.

**MS** [*m/z* (EI)]: 168 (M<sup>+</sup>, 37), 84 (53), 83 (60), 82 (36), 81 (23), 71 (32), 70 (54), 69 (100), 68 (25), 67 (28), 57 (59), 56 (41), 55 (84), 54 (23), 43 (51), 42 (22), 41 (95), 39 (40), 29 (36), 27 (23).

### 2-Pent-3-enyl-3,4-dihydro-2H-pyran

[0079]

**bp**<sub>0.1 Torr</sub>: 50-60 °C (Kugelrohr).

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) : 1.45-1.75 (m, 6H); 1.77-1.9 (m, 1H); 1.9-2.0 (m, 1H); 2.0-2.2 (m, 3H); 3.75-3.82 (m, 1H); 4.62-4.7 (m, 1H); 5.35-5.52 (m, 2H); 6.36 (d, 1H, *J* 8).

**IR** ( $\nu_{\max}$ : neat, cm<sup>-1</sup>) : 3060w, 2920m, 2851w, 1650m.

**MS** [*m/z* (EI)]: 152 (M<sup>+</sup>, 15), 95 (25), 81 (55), 79 (28), 68 (26), 67 (41), 57 (28), 55 (100), 53 (20), 41 (38), 39 (32), 29 (23).

## 5. Preparation of cyclic phenacyl acetals (fragrance precursors)

### Method A:

[0080] To a suspension of the hydroxy-acetophenone (10 mmol) in toluene (10 ml) was added the cyclic vinyl ether (2 eq.), followed by trifluoroacetic acid (2 or 3 drops, ~ 0.01 eq.). The mixture was heated at 50°C. When the reaction was finished (TLC, 2-3 hours), it was diluted with MTBE and poured into aq. NaHCO<sub>3</sub> (sat.). The aqueous phase was separated and extracted with MTBE, and the combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. The crude, obtained after evaporation of the solvents, was purified by chromatography (SiO<sub>2</sub>, EtOAc/Hexane) to afford the desired product as a colorless to pale yellow oil.

### Method B:

[0081] To a suspension of the hydroxy-acetophenone (10 mmol) in toluene (10 ml) were added the acetyl derivative derived from the fragrant lactone (5 mmol) and pyridine (3-4 drops, 0.1 eq.). The mixture was heated under reflux overnight. Then, it was poured into aq. NaHCO<sub>3</sub> (sat.) and the separated aqueous phase was extracted with MTBE. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. The crude, obtained after evaporation of the solvents, was purified by chromatography (SiO<sub>2</sub>, EtOAc/Hexane) to afford the desired product as a colorless to pale yellow oil.

**1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydro-naphtalen-2-yl)-2-(8-methyl-1-oxa-spiro[4.5]dec-2-yloxy)-ethanone (1)****[0082]** Obtained as a separable mixture of diastereomers (ratio 6:1) according to method A.<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

major diastereomer: 0.88 (d, 3H, *J* 6.8); 0.95-1.02 (m, 2H); 0.99 (d, 3H, *J* 6.8); 1.06 (s, 3H); 1.25 (s, 3H); 1.30 (s, 3H); 1.32 (s, 3H); 1.35-1.8 (m, 9H); 1.8-1.95 (m, 3H); 2.0-2.1 (m, 1H); 2.13-2.22 (m, 1H); 2.48 (s, 3H); 4.72 (m, 2H); 5.21 (m, 1H); 7.20 (s, 1H); 7.54 (s, 1H).

minor diastereomer: 0.9 (d, 3H, *J* 6.8); 0.9-1.02 (m, 2H); 0.99 (d, 3H, *J* 6.8); 1.07 (s, 3H); 1.27 (m, 3H); 1.32 (s, 3H); 1.33 (s, 3H); 1.25-1.8 (m, 9H); 1.82-2.0 (m, 3H); 2.0-2.2 (m, 2H); 2.54 (s, 3H); 4.67-4.8 (m, 2H); 5.38 (dd, 1H, *J* 4.8, 1.2); 7.21 (s, 1H); 7.56 (s, 1H).

IR (ν<sub>max</sub>: neat, cm<sup>-1</sup>): 2960m, 2925m, 1681m, 1607w, 1544w.UV [λ (ε), CH<sub>2</sub>Cl<sub>2</sub>, nm]: 217 (18273), 258 (10652).MS [m/z (EI)]: 426 (M<sup>+</sup>, 1), 258 (20), 244 (25), 243 (100), 153 (96), 152 (38), 135 (84), 81 (24), 69 (24), 67 (25), 55 (22), 43 (22), 41 (25).**2-(5-Heptyl-tetrahydro-furan-2-yloxy)-1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydro-naphtalen-2-yl)-ethanone (2)****[0083]** Obtained as a separable mixture of diastereomers (ratio 1:1) according to method A.<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

1<sup>st</sup> diastereomer: 0.87 (t, 3H, *J* 7.2); 0.99 (d, 3H, *J* 6.8); 1.06 (s, 3H); 1.26 (s, 3H); 1.31 (s, 3H); 1.32 (s, 3H); 1.2-1.5 (m, 12H); 1.55-1.7 (m, 2H); 1.8-1.95 (m, 2H); 2.0-2.15 (m, 3H); 2.48 (s, 3H); 3.9-4.0 (m, 1H); 4.65-4.75 (m, 2H); 5.25 (m, 1H); 7.2 (s, 1H); 7.56 (s, 1H).

2<sup>nd</sup> diastereomer: 0.87 (t, 3H, *J* 7.2); 0.99 (d, 3H, *J* 6.8); 1.06 (s, 3H); 1.26 (s, 3H); 1.31 (s, 3H); 1.32 (s, 3H); 1.2-1.5 (m, 12H); 1.55-1.7 (m, 2H); 1.8-2.05 (m, 4H); 2.48 (s, 3H); 4.0-4.1 (m, 1H); 4.65-4.8 (m, 2H); 5.2 (m, 1H); 7.21 (s, 1H); 7.55 (s, 1H).

IR (ν<sub>max</sub>: neat, cm<sup>-1</sup>): 2957m, 2926s, 2856m, 1684m, 1608w, 1545w.UV [λ (ε), CH<sub>2</sub>Cl<sub>2</sub>, nm]: 217 (14652), 258 (8060).MS [m/z (EI)]: 442 (M<sup>+</sup>), 258 (19), 244 (30), 243 (100), 169 (27), 95 (39), 81 (20), 69 (27).**2-(5-Heptyl-tetrahydro-furan-2-yloxy)-1-naphtalen-2-yl-ethanone (3)****[0084]** Obtained as a separable mixture of diastereomers (ratio 3:2) according to method A.<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

major diastereomer: 0.87 (t, 3H, *J* 6.8); 1.2-1.35 (m, 10H); 1.35-1.5 (m, 2H); 1.5-1.6 (m, 1H); 2.05-2.17 (m, 3H); 3.87 (s, 3H); 3.95-4.05 (m, 1H); 4.91 (d, 1H, *J* 16.8); 5.01 (d, 1H, *J* 16.8); 5.30 (dd, 1H, *J* 4.6, 1.4); 7.52-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.47 (s, 1H).

minor diastereomer: 0.85 (t, 3H, *J* 7); 1.2-1.5 (m, 10H); 1.55-1.7 (m, 2H); 1.7-1.82 (m, 1H); 1.95-2.05 (m, 2H); 2.17-2.25 (m, 1H); 4.0-4.1 (m, 1H); 4.90 (d, 1H, *J* 16.4); 5.03 (d, 1H, *J* 16.4); 5.25 (m, 1H); 7.52-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.47 (s, 1H).

IR (ν<sub>max</sub>: neat, cm<sup>-1</sup>): 2926s, 2855m, 1697s, 1628m, 1597w.

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**UV** [ $\lambda$  (e), CH<sub>2</sub>Cl<sub>2</sub>, nm] : 250 (54627), 284 (10571).

**MS** [m/z (EI)]: 354 (M<sup>+</sup>, 1), 170 (57), 169 (46), 155 (31), 151 (21), 141 (22), 127 (36), 109 (29), 95 (100), 83 (25), 81 (46), 69 (31), 67 (35), 57 (24), 55 (33), 43 (30), 41 (33).

### 2-(5-Heptyl-tetrahydro-furan-2-yloxy)-1-(4-methoxy-phenyl)-ethanone (4)

**[0085]** Obtained as a separable mixture of diastereomers (ratio 1:1) according to method B.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) :

1<sup>st</sup> diastereomer: 0.88 (t, 3H, *J* 7); 1.2-1.35 (m, 10H); 1.35-1.47 (m, 2H); 1.5-1.57 (m, 1H); 2.0-2.15 (m, 3H); 3.87 (s, 3H); 3.95-4.02 (m, 1H); 4.73 (d, 1H, *J* 16.4); 4.83 (d, 1H, *J* 16.4); 5.25 (m, 1H); 6.91-6.95 (m, 2H); 7.91-7.95 (m, 2H).

2<sup>nd</sup> diastereomer: 0.88 (t, 3H, *J* 7); 1.2-1.5 (m, 11H); 1.57-1.65 (m, 1H); 1.7-1.8 (m, 1H); 1.9-2.02 (m, 2H); 2.15-2.22 (m, 1H); 3.87 (s, 3H); 4.0-4.1 (m, 1H); 4.72 (d, 1H, *J* 16); 4.84 (d, 1H, *J* 16); 5.19 (m, 1H); 6.91-6.95 (m, 2H); 7.91-7.95 (m, 2H).

**IR** ( $\nu_{\max}$ : neat, cm<sup>-1</sup>) : 2927m, 2855m, 1777w, 1693m, 1601s, 1576m.

**UV** [ $\lambda$  (e), CH<sub>2</sub>Cl<sub>2</sub>, nm] : 218 (5724), 272 (8235).

**MS** [m/z (EI)]: 334 (M<sup>+</sup>), 169 (31), 151 (26), 150 (78), 135 (71), 109 (24), 95 (100), 81 (37), 69 (22), 67 (22), 55 (20).

### 1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydro-naphthalen-2-yl)-2-(6-pent-3-enyl-tetrahydro-pyran-2-yloxy)-ethanone (5)

**[0086]** Obtained as a mixture of diastereomers according to method A.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) :

major diastereomer: 0.99 (d, 3H, *J* 6.8); 1.07 (s, 3H); 1.26 (s, 3H); 1.31 (s, 3H); 1.33 (s, 3H); 1.37-1.7 (m, 11H); 1.8-2.2 (m, 5H); 2.19 (s, 3H); 3.7-3.8 (m, 1H); 4.73 (s, 2H); 4.97 (m, 1H); 5.34-5.5 (m, 2H); 7.22 (s, 1H); 7.57 (s, 1H).

**IR** ( $\nu_{\max}$ : neat, cm<sup>-1</sup>) : 2934s, 1698m, 1608w.

**UV** [ $\lambda$  (e), CH<sub>2</sub>Cl<sub>2</sub>, nm] : 213 (15336), 258 (8487).

**MS** [m/z (EI)]: 426 (M<sup>+</sup>, 1), 243 (100), 153 (18), 135 (43), 85 (33), 55(25).

### 1-(Naphthalen-2-yl)-2-(6-pent-3-enyl-tetrahydro-pyran-2-yloxy)-ethanone (6)

**[0087]** Obtained as a separable mixture of diastereomers (ratio 19:1) according to method A.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):

major diastereomer: 1.4-1.75 (m, 9H); 1.9-2.2 (m, 4H); 3.75-3.82 (m, 1H); 4.9-5.05 (m, 3H); 5.35-5.5 (m, 2H); 7.55-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.47 (s, 1H).

minor diastereomer: 1.4-1.75 (m, 9H); 1.9-2.2 (m, 4H); 3.3-3.4 (m, 1H); 5.0-5.2 (m, 3H); 5.35-5.5 (m, 2H); 7.55-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.49 (s, 1H).

**IR** ( $\nu_{\max}$ : neat, cm<sup>-1</sup>) : 2936m, 1697s, 1628m, 1596w.

**UV** [ $\lambda$  (e), CH<sub>2</sub>Cl<sub>2</sub>, nm] : 250 (45352), 285 (8887).

**MS** [m/z (EI)]: 338 (M<sup>+</sup>, 4), 186 (22), 170 (100), 155 (79), 153 (37), 141 (26), 135 (83), 127 (64), 109 (32), 107 (27), 96 (24), 93 (37), 85 (69), 81 (31), 79 (30), 69 (43), 67 (40), 57 (26), 55 (70), 41 (21).

**Example 2**

**[0088]** Photolysis of cyclic phenacyl acetals (I) in solutions

**[0089]** Photorelease assays were conducted on solutions (typical concentrations of precursors (I): 0.05% to 0.1% g/v) in organic solvents (preferably ethanol) or on cotton towels after deposition of the phenacyl acetals (I), as described below in the example 3.

**[0090]** The solutions were irradiated with a mercury lamp (150 W) in a borosilicate glass apparatus (Pyrex®) so as to limit the irradiation window to mainly the UVA and UVB spectrum of sun light. The alcoholic solution was irradiated for one hour and samples taken every 15 min to analyze the extent of the photolysis.

**Analysis**

**[0091]** The presence of the aryl ketone (II) and lactone (III) after photolysis in solutions was determined by using GC retention times. Samples (0.2 µl) were injected (on column injection) without further dilution. Gas chromatography/flame ionisation detection (GC-FID) was carried out with a Fisons-GC 8000series apparatus, using a *J&W Scientific* DB-5 capillary column (30m, 0.32mm id, 0.25µm film, He carrier gas, 85 kPa). The results are summarized in table 1.

**[0092]** Whereas precursors derived from Oranger Crystals® cleaved fairly slowly, those derived from Fixolide® cleaved fast and acetanisol precursors even faster. The estimated half lives under the said conditions were inferred from the GC analysis (corresponding peak area).

$$t_{1/2} \text{ (Acetanisol)} = 7\text{-}8 \text{ min}$$

$$t_{1/2} \text{ (Fixolide®)} = 6\text{-}7 \text{ min}$$

$$t_{1/2} \text{ (Oranger Crystals®)} = 30\text{-}35 \text{ min}$$



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15

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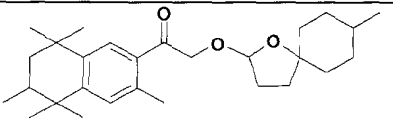
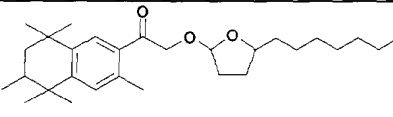
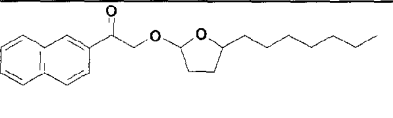
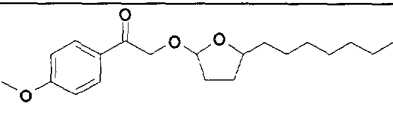
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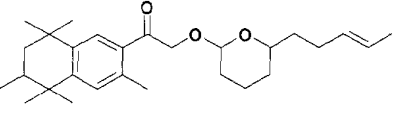
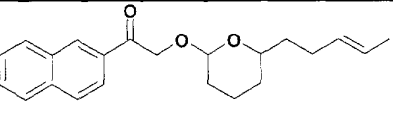
## 30

## 45

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**Table 2:** Release of aryl ketones and lactones from cyclic phenacyl acetals on fabric upon irradiation with a tanning lamp.

	STRUCTURE	Fragrance (perception) *	Target	Global appre- ciation*
		aryl ketone (II)	lactone (III)	
<b>1</b>		Fixolide® (++)	Methyl Laitone® (+)	+
<b>2</b>		Fixolide® (++)	Peach Pure® (++)	++
<b>3</b>		Oranger Crystals® (++)	Peach Pure® (++)	++
<b>4</b>		Acetanisol (++)	Peach Pure® (++)	+++

<b>5</b>		Fixolide® (++)	Jasmolactone® (+++)	+++
<b>6</b>		Oranger Crystals® (++)	Jasmolactone® (++)	++

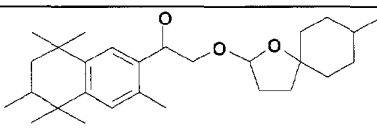
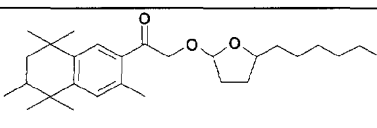
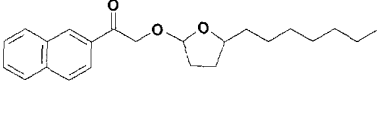
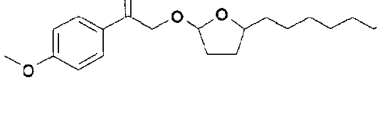
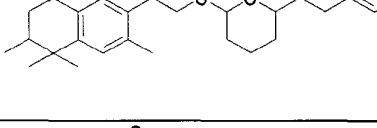
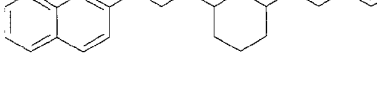
\* 0 : very weak, + : weak, ++ : medium, +++ : strong

## Example 4

## Stability tests

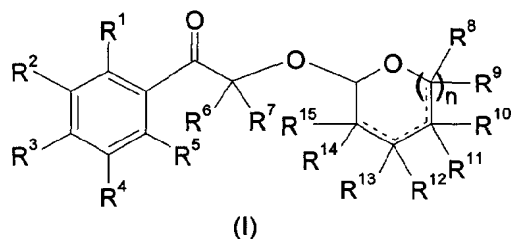
[0094] The cyclic phenacyl acetals (I) were incubated in aqueous buffer solutions of pH 2.5, pH 7 and pH 9.5 for 24h at 37 °C and were found to be stable in basic and neutral media, but less so under acidic conditions. The results are summarised in table 3.

**Table 2:** Stability of cyclic phenacyl acetals under different pH

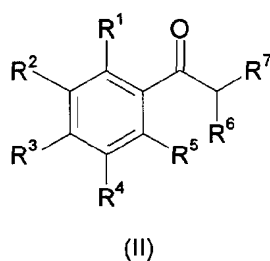
	STRUCTURE	pH 2.5	pH 7	pH 9.5
1		stable	stable	stable
2		stable	stable	stable
3		unstable	stable	stable
4		unstable	stable	stable
5		stable	stable	stable
6		unstable	stable	stable

## Claims

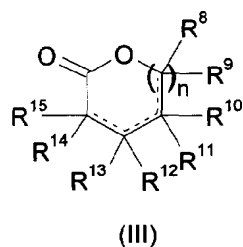
1. Fragrance precursors of formula I



the dotted lines indicating one or two optional double bonds in the cyclic acetal  
for a fragrant ketone of formula II



and a fragrant lactone of formula III



containing not more than 20 carbon atoms,  
wherein

R<sup>1</sup> to R<sup>5</sup> represent independently H, -NO<sub>2</sub>, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl or C<sub>1</sub>-C<sub>4</sub>-alkoxy,

R<sup>1</sup> and R<sup>2</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>3</sup> and R<sup>4</sup> and R<sup>4</sup> and R<sup>5</sup> may form together one or two aliphatic or aromatic rings, these rings may optionally contain linear or branched C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkenyl or C<sub>1</sub>-C<sub>4</sub>-alkynyl residues, and these rings and residues may comprise one or more oxygen atoms,

R<sup>6</sup> and R<sup>7</sup> are independently H, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl-, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, and R<sup>6</sup> or R<sup>7</sup> may form with either R<sup>1</sup> or R<sup>5</sup> a carbocyclic ring optionally substituted by an aliphatic residue,

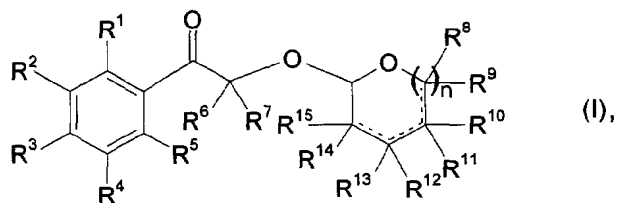
n is either 0 or 1,

R<sup>8</sup> to R<sup>15</sup> are independently H, branched or linear C<sub>1</sub>-C<sub>15</sub>-alkyl, C<sub>1</sub>-C<sub>15</sub>-alkenyl, C<sub>1</sub>-C<sub>15</sub>-alkynyl or C<sub>1</sub>-C<sub>4</sub>-alkoxy, they may form together one or more aliphatic or aromatic rings, these rings may optionally contain branched or linear C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>1</sub>-C<sub>10</sub>-alkenyl or C<sub>1</sub>-C<sub>10</sub>-alkynyl residues, and these rings and residues may

comprise one or more oxygen atoms.

2. Fragrance precursors of formula I according to claim 1, wherein  $n = 0$ , one of the residues  $R^{11}$  to  $R^{15}$  being an aliphatic residue having 1 to 15 carbon atoms and the others being H.
3. Fragrance precursors of formula I according to one of the claims 1 to 2, wherein  $n = 0$ ,  $R^{10}$  is an aliphatic residue having 1 to 15 carbon atoms and  $R^{11}$  to  $R^{15}$  are H.
4. Fragrance precursors of formula I according to one of the claims 1 to 3, wherein  $n = 0$ , two or more of the residues  $R^{10}$  to  $R^{15}$  being aliphatic residues having 1 to 15 carbon atoms and the others being H.
5. Fragrance precursors of formula I according to one of the claims 1 to 4, wherein  $n = 0$  and  $R^{10}$  and  $R^{11}$  being aliphatic residues having 1 to 10 carbon atoms.
6. Fragrance precursors of formula I according to one of the claims 1 to 5, wherein  $n = 0$  and at least two of the residues  $R^{10}$  to  $R^{15}$  are residues having 1 to 15 carbon atoms and form together one or more carbocyclic ring(s), which may optionally be substituted with one or more aliphatic residue(s) having 1 to 10 carbon atoms.
7. Fragrance precursors of formula I according to one of the claims 1 to 6, wherein  $n = 0$  and  $R^{10}$  and  $R^{11}$  are residues having 1 to 15 carbon atoms form together a ring which may be further substituted with one or more aliphatic residues having 1 to 10 carbon atoms.
8. Fragrance precursors of formula I according to one of the claims 1 to 7, wherein  $n = 1$ , one or more of the residues  $R^8$  to  $R^{15}$  being an aliphatic residue having 1 to 15 carbon atoms the others being H.
9. Fragrance precursors of formula I according to one of the claims 1 to 8, wherein  $n = 1$ ,  $R^8$  is an aliphatic residue having 1 to 15 carbon atoms and  $R^9$  to  $R^{15}$  are H.
10. Fragrance precursors of formula I according to one of the claims 1 to 9, wherein  $n = 1$ , at least two of the residues  $R^8$  to  $R^{15}$  are aliphatic having 1 to 15 carbon atoms and the other residues are H.
11. Fragrance precursors of formula I according to one of the claims 1 to 10, wherein  $n = 1$  and at least two of the residue  $R^8$  to  $R^{15}$  are residues having 1 to 15 carbon atoms and form together one or more carbocyclic ring(s), which may optionally be substituted with one or more aliphatic residues having 1 to 10 carbon atoms.
12. Fragrance precursors of formula I according to one of the claims 1 to 11, wherein at least one of the residues  $R^6$  and  $R^7$  is H.
13. Fragrance precursors of formula I according to one of the claims 1 to 12, wherein the residues  $R^6$  and  $R^7$  are H.
14. Fragrance precursors of formula I according to one of the claims 1 to 13, wherein the residues  $R^6$  and  $R^7$  are H and  $R^1$  to  $R^5$  represent independently H,  $-\text{NO}_2$ , linear or branched  $\text{C}_1\text{-C}_6$ -alkyl,  $\text{C}_1\text{-C}_6$ -alkenyl,  $\text{C}_1\text{-C}_6$ -alkynyl or  $\text{C}_1\text{-C}_4$  alkoxy.
15. Fragrance precursors of formula I according to one of the claims 1 to 14, wherein the fragrant ketone of formula II is selected from 1-phenyl-ethanone, 2,4-dimethylphenyl-ethanone, 1-[4-(1,1-dimethylethyl)-2,6-dimethylphenyl]-ethanone, 1-(4-tert-butyl-3,5-dinitro-2,6-dimethyl)-ethanone and 1-(4-methoxy-phenyl)-ethanone.
16. Fragrance precursors of formula I according to one of the claims 1 to 15, wherein  $R^1$  and  $R^2$ ,  $R^2$  and  $R^3$ ,  $R^3$  and  $R^4$ , and  $R^4$  and  $R^5$ , form together one or two aliphatic or aromatic rings which may optionally contain substituted or unsubstituted  $\text{C}_1\text{-C}_4$ -alkyl,  $\text{C}_1\text{-C}_4$ -alkenyl,  $\text{C}_1\text{-C}_4$ -alkynyl residues and may comprise one or more oxygen atoms.
17. Fragrance precursors of formula I according to one of the claims 1 to 16, wherein the fragrant ketone of formula II is selected from 1-(2-naphthalenyl)-ethanone, 4-acetyl-6-tert-butyl-1,1-dimethyl-indan, 1-(5,6,7,8-tetrahydro-3',5',5',6',8',8'-hexamethyl-2-naphthalenyl)-ethanone, 1-(5,6,7,8-tetrahydro-3',5',5',8',8'-pentamethyl-2-naphthalenyl)-ethanone, 1-(5,6,7,8-tetrahydro-3'-ethyl-5',5',8',8'-tetra-methyl-2-naphthalenyl)-ethanone, 1-(2,3-dihydro-1',1',2',3',3',6'-hexamethyl-1H-inden-5-yl)-ethanone, 1-[2,3-dihydro-1',1',2',6'-tetramethyl-3-(1-methyl-ethyl)-1H-inden-5-yl]-ethanone, 5-acetyl-1,1,2,3,3-pentamethyl-indane, 1-(5,6,7,8-tetrahydro-2-naphthalenyl)-ethanone.

## 18. Compounds of formula I



the dotted lines indicating one or two double bonds in the ring of the cyclic acetal, wherein

R<sup>1</sup> to R<sup>5</sup> represent independently H, -NO<sub>2</sub>, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, or C<sub>1</sub>-C<sub>4</sub>-alkoxy,

R<sup>1</sup> and R<sup>2</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>3</sup> and R<sup>4</sup> and R<sup>4</sup> and R<sup>5</sup> may form together one or two aliphatic or aromatic rings, these rings may optionally contain substituted or unsubstituted C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkenyl or C<sub>1</sub>-C<sub>4</sub>-alkynyl residues, and may comprise one or more oxygen atoms,

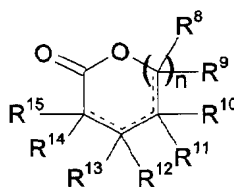
R<sup>6</sup> and R<sup>7</sup> are independently H, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, and R<sup>6</sup> or R<sup>7</sup> may form with either R<sup>1</sup> or R<sup>5</sup> a substituted or unsubstituted carbocyclic ring,

n is either 0 or 1,

R<sup>8</sup> to R<sup>15</sup> are independently H, branched or linear C<sub>1</sub>-C<sub>15</sub>-alkyl, C<sub>1</sub>-C<sub>15</sub>-alkenyl, C<sub>1</sub>-C<sub>15</sub>-alkynyl or C<sub>1</sub>-C<sub>4</sub>-alkoxy, they may form together one or more aliphatic or aromatic rings, these rings may optionally contain branched or linear C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>1</sub>-C<sub>10</sub>-alkenyl or C<sub>1</sub>-C<sub>10</sub>-alkynyl residues, and the above rings and residues may comprise one or more oxygen atoms,

and

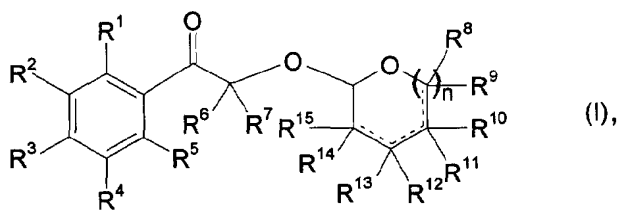
the lactone of formula III



(III)

contains not more than 20 carbon atoms.

## 19. Compounds of formula I



wherein

the ring of the acetal is saturated,

R<sup>1</sup> to R<sup>5</sup> represent independently H, -NO<sub>2</sub>, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, or C<sub>1</sub>-C<sub>4</sub>-alkoxy,

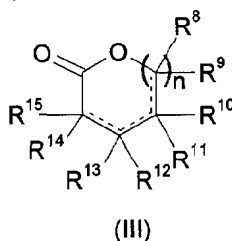
R<sup>1</sup> and R<sup>2</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>3</sup> and R<sup>4</sup> and R<sup>4</sup> and R<sup>5</sup> may form together one or two aliphatic or aromatic rings, these rings may optionally contain substituted or unsubstituted C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkenyl or C<sub>1</sub>-C<sub>4</sub>-alkynyl residues, and may comprise one or more oxygen atoms,

R<sup>6</sup> and R<sup>7</sup> are independently H, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, and R<sup>6</sup> or R<sup>7</sup> may form with either R<sup>1</sup> or R<sup>5</sup> a substituted or unsubstituted carbocyclic ring,

n is 0,

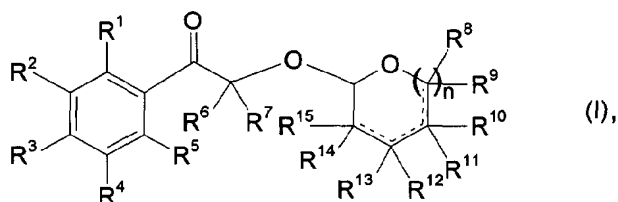
R<sup>8</sup> to R<sup>15</sup> are independently H, branched or linear C<sub>1</sub>-C<sub>15</sub>-alkyl, C<sub>1</sub>-C<sub>15</sub>-alkenyl, C<sub>1</sub>-C<sub>15</sub>-alkynyl or C<sub>1</sub>-C<sub>4</sub>-alkoxy, they may form together one aliphatic or aromatic ring, and the ring may optionally contain branched or linear C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>1</sub>-C<sub>10</sub>-alkenyl or C<sub>1</sub>-C<sub>10</sub>-alkynyl residues, and the above rings and residues may comprise one or more oxygen atoms, and

the lactone of formula III



contains not more than 20 carbon atoms.

## 20. Compounds of formula I



wherein

the ring of the acetal is saturated,

R<sup>1</sup> to R<sup>5</sup> represent independently H, -NO<sub>2</sub>, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, or C<sub>1</sub>-C<sub>4</sub>-alkoxy,

R<sup>1</sup> and R<sup>2</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>3</sup> and R<sup>4</sup> and R<sup>4</sup> and R<sup>5</sup> may form together one or two aliphatic or aromatic rings, these rings may optionally contain substituted or unsubstituted C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkenyl or C<sub>1</sub>-C<sub>4</sub>-alkynyl residues, and may comprise one or more oxygen atoms,

R<sup>6</sup> and R<sup>7</sup> are independently H, linear or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl, C<sub>1</sub>-C<sub>6</sub>-alkynyl, and R<sup>6</sup> or R<sup>7</sup>

may form with either R<sup>1</sup> or R<sup>5</sup> a substituted or unsubstituted carbocyclic ring,  
n is 1,

R<sup>8</sup> to R<sup>15</sup> are independently H, branched or linear C<sub>1</sub>-C<sub>15</sub>-alkyl, C<sub>1</sub>-C<sub>15</sub>-alkynyl or C<sub>1</sub>-C<sub>4</sub>-alkoxy, they may form together one or more aliphatic or aromatic rings, these rings may optionally contain branched or linear C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>1</sub>-C<sub>10</sub>-alkenyl or C<sub>1</sub>-C<sub>10</sub>-alkynyl residues, and the above rings and residues may comprise one or more oxygen atoms,

with the proviso that compounds

wherein

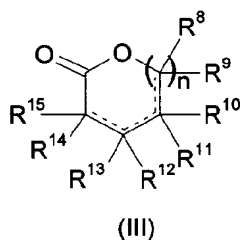
all of R<sup>8</sup> to R<sup>15</sup> are H,

or

all of R<sup>10</sup> to R<sup>15</sup> are H and either R<sup>8</sup> is C<sub>6</sub> and R<sup>9</sup> is H or R<sup>9</sup> is C<sub>6</sub> and R<sup>8</sup> is H are excluded,

and

the lactone of formula III



contains not more than 20 carbon atoms.

21. Perfumed products comprising fragrance precursors of formula I according to one of the claims 1 to 17.
22. Perfumed products comprising fragrance precursors of formula I according to claim 21, being laundry compositions, cleaning products, body care products or personal care products.
23. Use of perfumed products comprising fragrance precursors of formula I according to one of the claims 1 to 17 as laundry compositions, cleaning products, body care products or personal care products.





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 00 11 1981

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Place of search <b>MUNICH</b>		Date of completion of the search <b>17 November 2000</b>	Examiner <b>Helps, I</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/82 (F04C01)



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Application Number  
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<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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